

INVESTIGATIONS ON THE STRUCTURAL
PROPERTIES OF LIME

BY

PETER MICHAEL BERNAYS

S.B., Massachusetts Institute of Technology, 1939

M.S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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INTRODUCTION

The lime industry, one of the oldest chemical industries in the United States, has always used empirical methods to control and operate its process. Each plant produces a different product, and there have never been any methods with which to settle competitive problems. High calcium materials claimed superiority over dolomitic products, and the latter field was split on the question of complete hydration of magnesia as well as calcia.

The lime producer needs a rapid method of determining what phases are present in his material. The possible phases include calcium oxide, magnesium oxide, calcium hydroxide, magnesium hydroxide, calcium carbonate, magnesium carbonate, dolomite, and magnesium carbonate trihydrate. These must be distinguished both qualitatively and quantitatively. Chemical methods will not suffice in this case, for a chemical analysis, even if it could be done in rapid time, would lead to several possible interpretations.

The first objective in this thesis investigation has been to adopt the x-ray diffraction method to a qualitative and quantitative analysis of the constituents present in any lime sample, both for fundamental study of reactions which may occur under a wide range of conditions and for practical and routine utilization in the industry. With the possible exception of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ all of the above mentioned compounds have crystal structures which have been determined previously. Consequently standard patterns of single pure compounds could be carefully checked against data recorded in the literature. No information has been available previously, however, on mixtures of two or more of these compounds, upon the limits of detection of one phase in the presence of others, on the possibility of formation of complex compounds, higher hydrates, etc. The obvious extension of this technique is the

analysis of very old mortars since something of the origin and history of such samples can be deduced.

A second objective has been the extension of x-ray diffraction and related methods to the study of the *texture* of lime samples as a function of such variables as original raw material composition, temperature, time and mechanics of calcination; rate, degree, and mechanism of hydration; and plastic properties of mortars.

A few preliminary experiments in this Laboratory¹ indicated that particle size and shape are determined by the conditions of calcination of limestone (hardburned, softburned high calcium limes). Such methods have been further projected and extended to dolomitic limes, in which the properties of CaO and MgO are simultaneously involved.

RESULTS

Using a newly designed x-ray diffraction tube, methods have been developed to determine the nature of a dolomitic burn. Large particle size in the material under investigation leads to a speckling of the x-ray diffraction lines. A hardburned material has large particles, formed by prolonged heating at high temperatures. So the x-ray method can be adopted to determine the degree of burn of a dolomitic lime. In an extremely hardburned sample, even the MgO diffraction lines will be speckled, while in a normal hardburned material there will be speckling of CaO lines, and after extreme softburning, by calcination in steam² at 700° C., there will be no speckling, but a broadening of diffraction lines, caused by active, distorted, perhaps colloidal MgO and CaO.

Hydration of a dolomitic lime involves the formation of calcium hydroxide, and perhaps magnesium hydroxide. X-ray diffraction methods lead readily to an evaluation of materials present, and to an estimation of amounts. Thus it was found that a hardburned material, after hydration in air for a period of two months, still contained some MgO, although some hydroxide had been formed. On the other hand, an extremely softburned material, after steam hydration for two hours,

contained almost no magnesium oxide. In this way, all intermediate steps in hydration could be determined, and rates of hydration followed. It was an obvious outcome of this phase of the investigation, that active distorted MgO would hydrate readily, and without the extreme conditions necessary in industry.

Phases in the burn from different kilns are readily evaluated. The rotary material appears more uniform in composition, with little or no core, whereas the shaft material contains some hard- some softburned lime. Likewise, it is easy to follow the action of CO_2 and H_2O upon limes that are allowed to stand in such an environment for a long time. $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is the first product, and it is found that magnesium compounds slow up the rate of reaction of calcium compounds.

Old mortars and plasters, as mentioned above, are easily investigated by x-ray diffraction methods. Even after several hundred years, mortars may still contain calcium hydroxide. After forty years dolomitic plasters still contain MgO, and very little, if any, carbonate.

Texture is best studied by a knowledge of particle size and shape. By an evaluation of the width of an x-ray line, and the application of certain well known formulas the size of a particle can be found. If the size determined by measuring the breadth of several lines is the same, it is to be concluded that the particle is spherical or cubic. If, on the other hand, the sizes determined from various lines are different, it is to be concluded that the material is no longer equiaxed. By then determining which directions in the crystal lead to which sizes, it can be found whether or not the material is needle-like, flake-like, or what.

Applying this method to calcium and magnesium hydroxides, which have a layer lattice structure, one finds that these materials have a flake-like nature. By a measurement of the 001 and 111 diffraction lines the thickness and expanse of the flake can be determined. Further, lime is plastic because of the ready slippage of flake over flake. Thus thin flat particles are the most plastic. The excessive conditions imposed upon

lime to completely hydrate the magnesia have a detrimental effect upon the flake-like structure of the calcium hydroxide. In all cases studied, pressure processes had the effect of coarsening the calcium hydroxide, and making it more nearly cubic or spherical, therefore, less plastic. Thus a series of samples which are being studied concurrently at M.I.T., were evaluated and their plasticity estimated.

The lime producer is thus faced with the problems of weighing the added effect of complete hydration (less flaking upon drying as plaster) against the better plasticity of incomplete hydration. It appears necessary always to strike an optimum condition among opposing variables. For without x-ray examination it cannot be known whether, if the calcium is well-burned, the magnesia is hurt; or whether, if the magnesia is hydrated by drastic methods, harm is done to the calcium portion of the lime.

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VITA

The author was born July 19, 1918 in New York City. He received his elementary education in the public schools of Vienna, Austria, and New Rochelle, N.Y., as well as at the Walden School in New York City. After graduation from the New Rochelle High School in June 1935, he entered M.I.T. Here he received his Bachelor of Science in Chemistry in June 1939. In the fall of 1939 he entered the Graduate School of the University of Illinois, receiving his Master of Science in Chemistry in June 1940. During the school year 1940-1941 he held the National Lime Association Fellowship, and for the first semester of 1941-1942 he held a University Fellowship. He resigned the latter in order to become an Assistant Investigator for the National Defense Research Committee.

He is a member of Phi Beta Kappa, Sigma Xi, Phi Lambda Upsilon, the American Chemical Society, and Pi Lambda Phi.

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